

Improving Risk Assessments By Measuring Hydrocarbon Availability:

The Lampblack Experience

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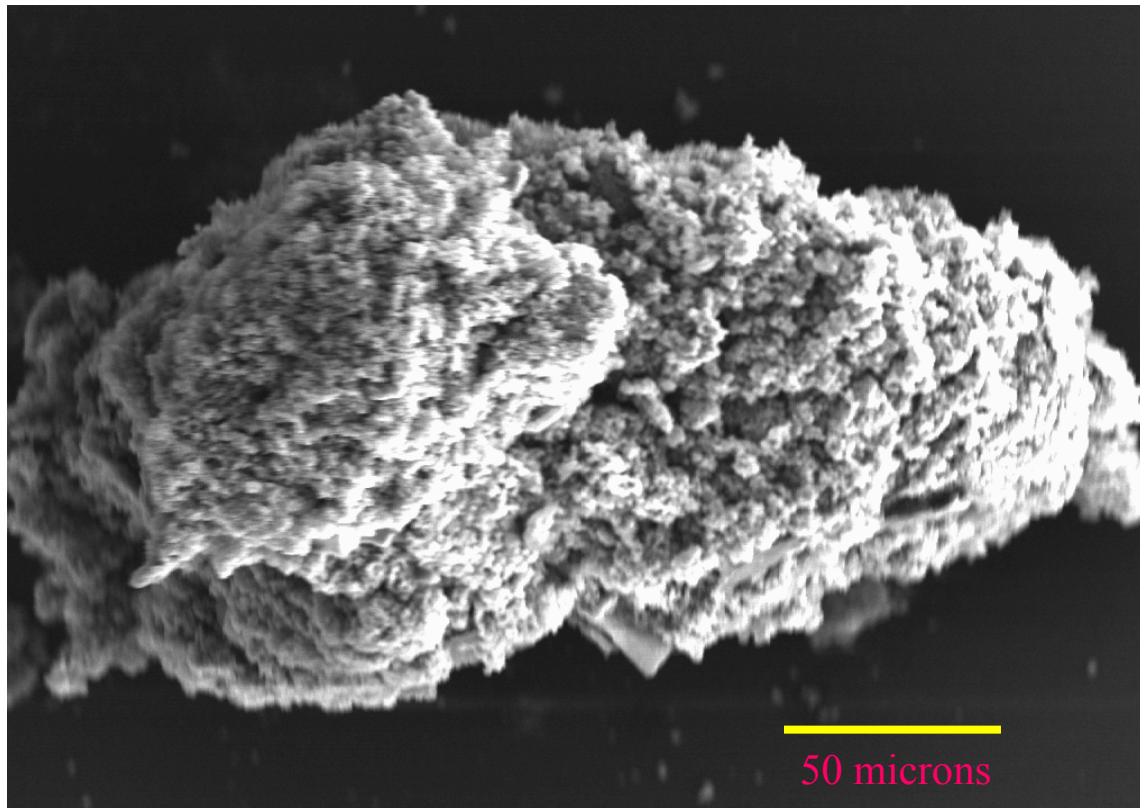
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Lampblack: A Matrix That Strongly Binds PAHs

- **Lampblack: Soot produced by oil combustion**
- **Large volumes of lampblack at CA MGP sites**
- **Lampblack can be over 80% Carbon**
- **Composed of “hard” (aromatic) Carbon (very little polar or alkane hydrocarbons)**
- **Has sorption characteristics similar to GAC**
- **Previous studies showed PAHs in lampblack (Santa Barbara sample) were not leachable and were not available for biological uptake**

Lampblack

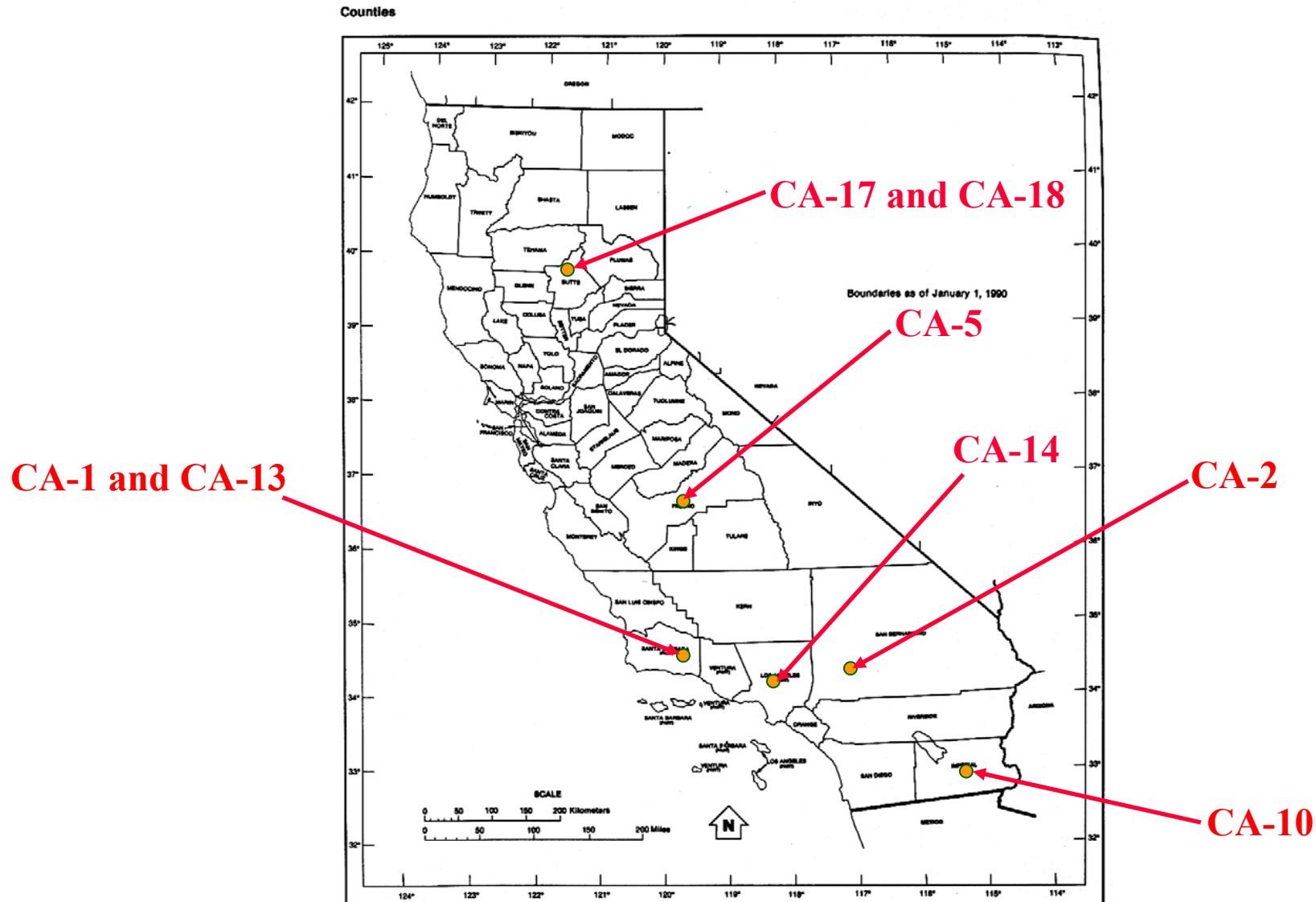
- SEM picture showing spongy nature of lampblack
- Sorption capacity and binding energy similar to soot



400 x

Sample CA-5

8 Lampblack Samples Tested, Representing Range of Compositions and Concentrations

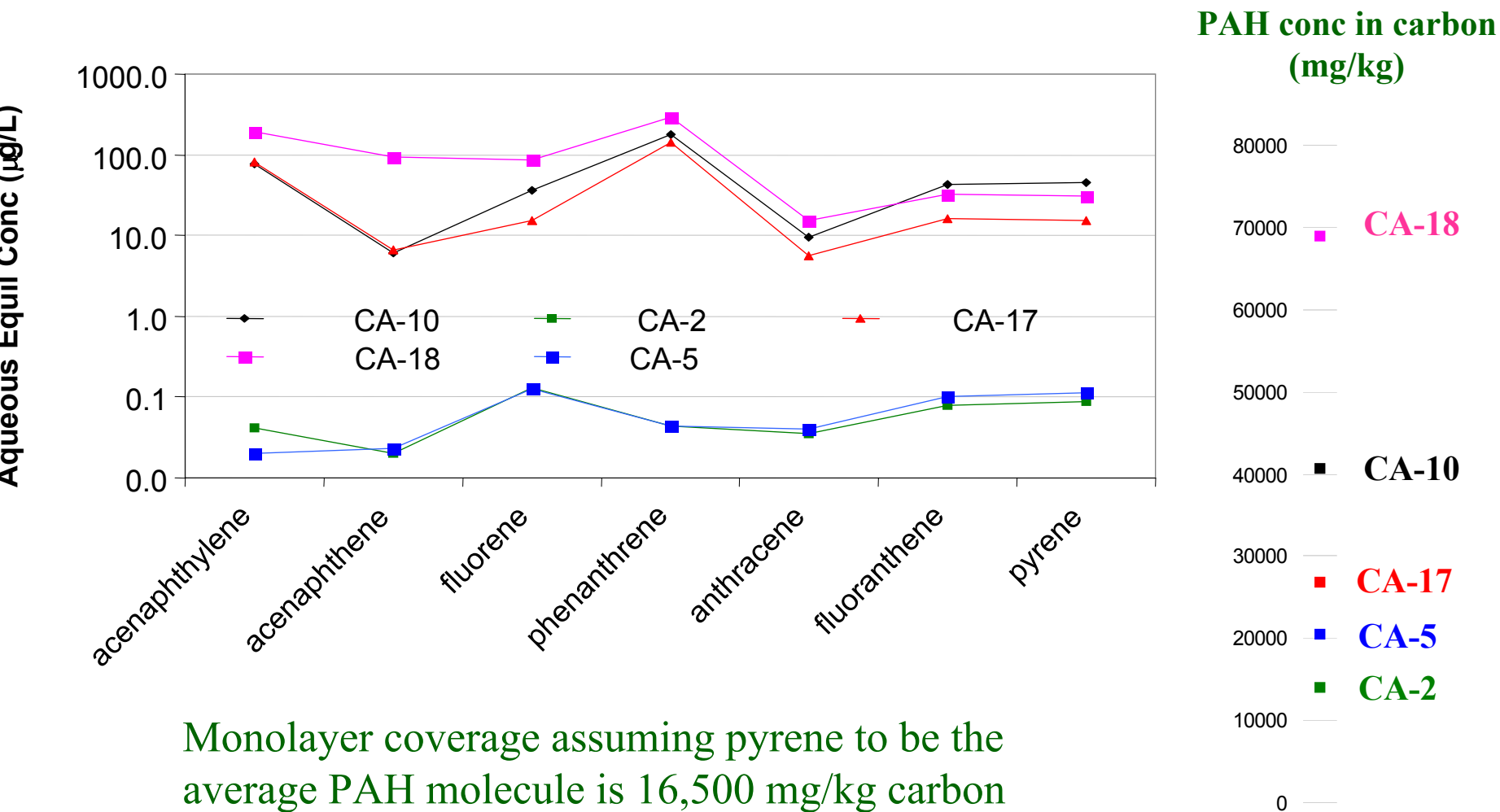


CA Risk Evaluation

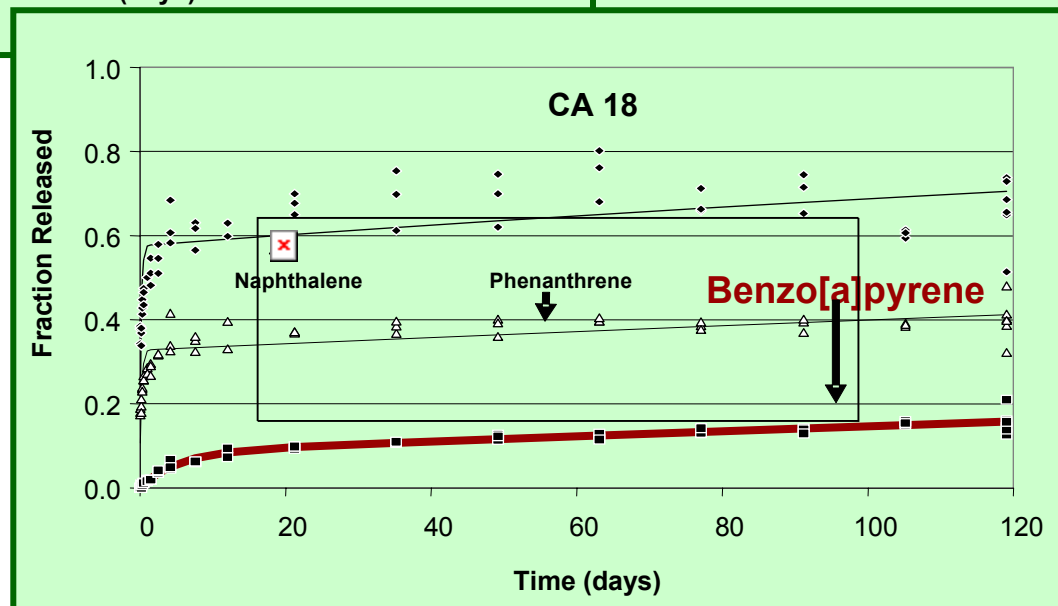
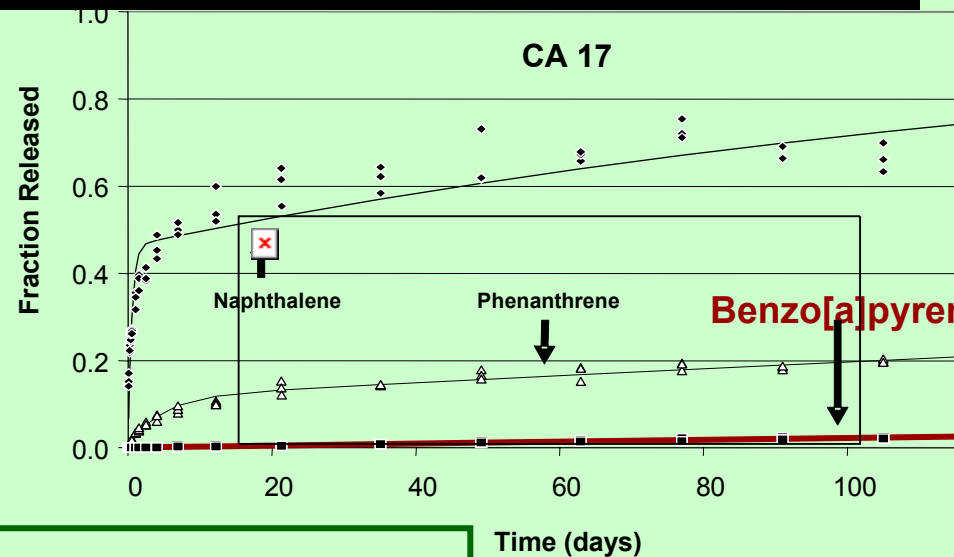
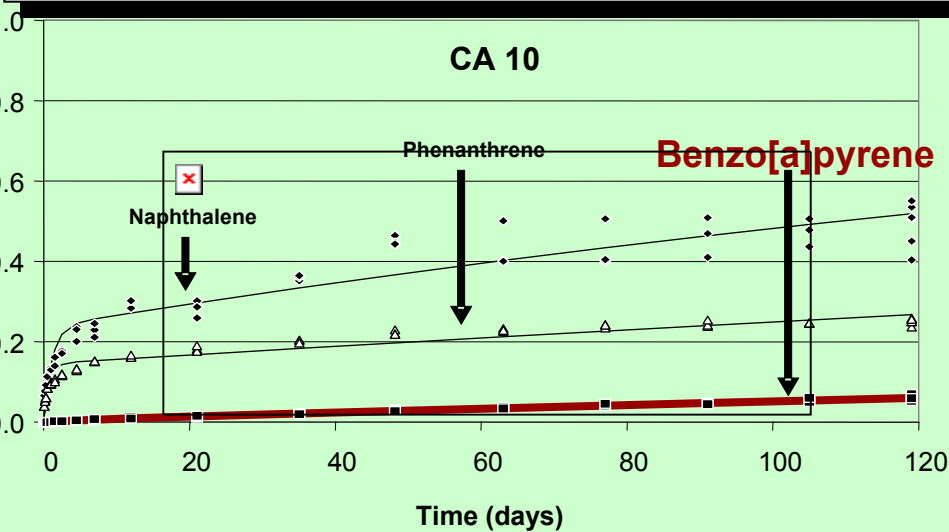
$$\begin{aligned} \text{Risk}_{\text{soil}} = & \text{SFo} \times \text{Cs} \times [(\text{IR}_s \times \text{EF} \times \text{ED} \times 10^{-6} \\ & \text{kg/mg}) / (\text{BW} \times \text{AT} \times 365 \text{ days/yr})]_{\text{child and adult}} \quad \left. \vphantom{\text{Risk}_{\text{soil}}} \right\} \text{Oral Risk} \\ & + \text{SFo} \times \text{Cs} \times [(\text{SA} \times \text{AF} \times \underline{\text{ABS}} \times \text{ED} \times 10^{-6} \\ & \text{kg/mg}) / (\text{BW} \times \text{AT} \times 365 \text{ days/yr})]_{\text{child and adult}} \quad \left. \vphantom{\text{Risk}_{\text{soil}}} \right\} \text{Dermal Risk} \end{aligned}$$

- **Bioavailability Factors Assumed**
 - **Oral bioavailability: 1 for any chemical**
 - **Dermal bioavailability (ABS): 0.15 for PAHs**
- **Objectives**
 - **Derive more realistic bioavailability values**
 - **Develop protocols to measure bioavailability of PAHs in lampblack**

Measured Equilibrium Concentrations May Be Less Than 0.1 ppb



Less Than 20% of the B[a]P is Released in Over 4 Months of Water Extraction

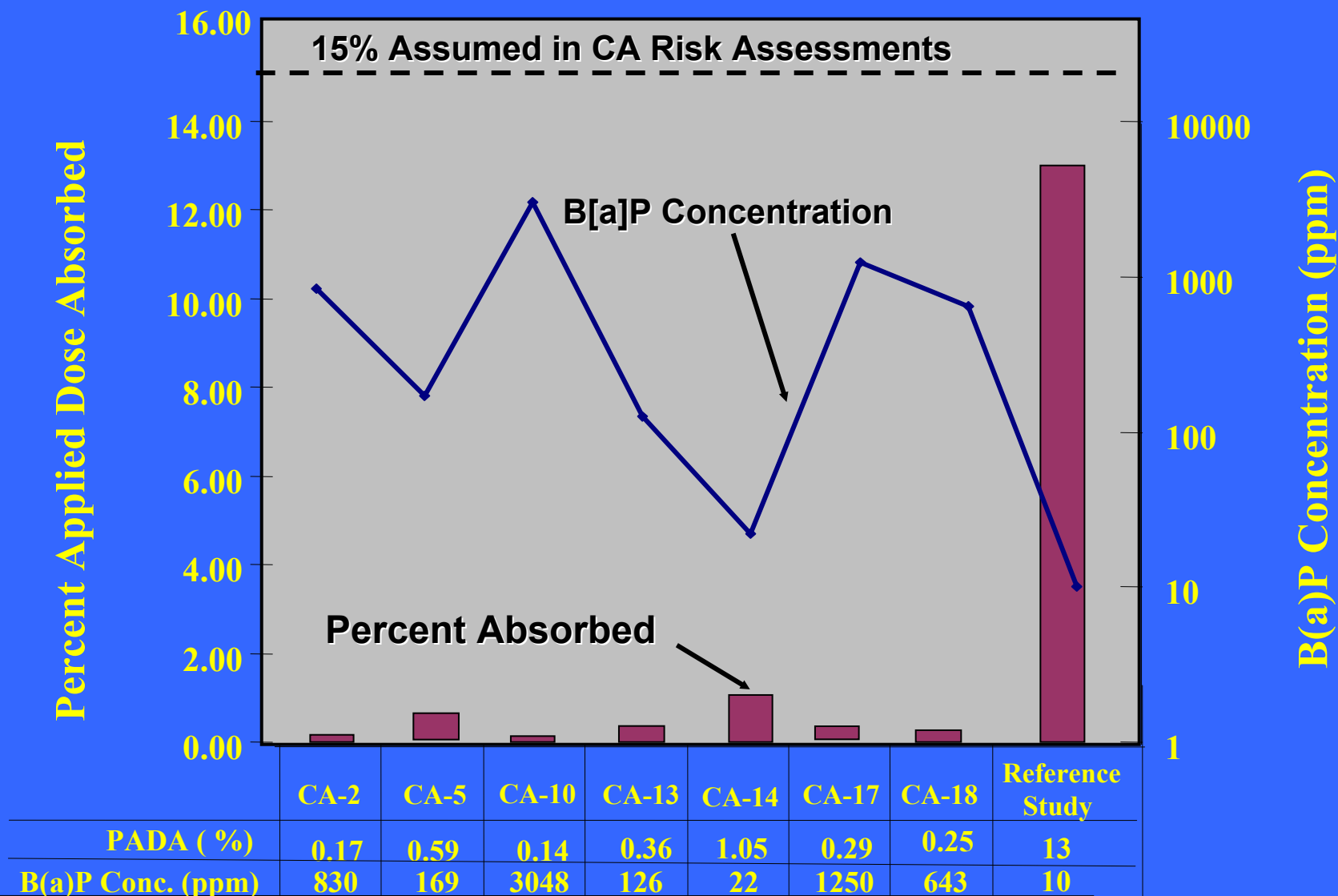


UPTAKE OF NATIVE PAHs AND DEUTERATED SPIKED PAHs

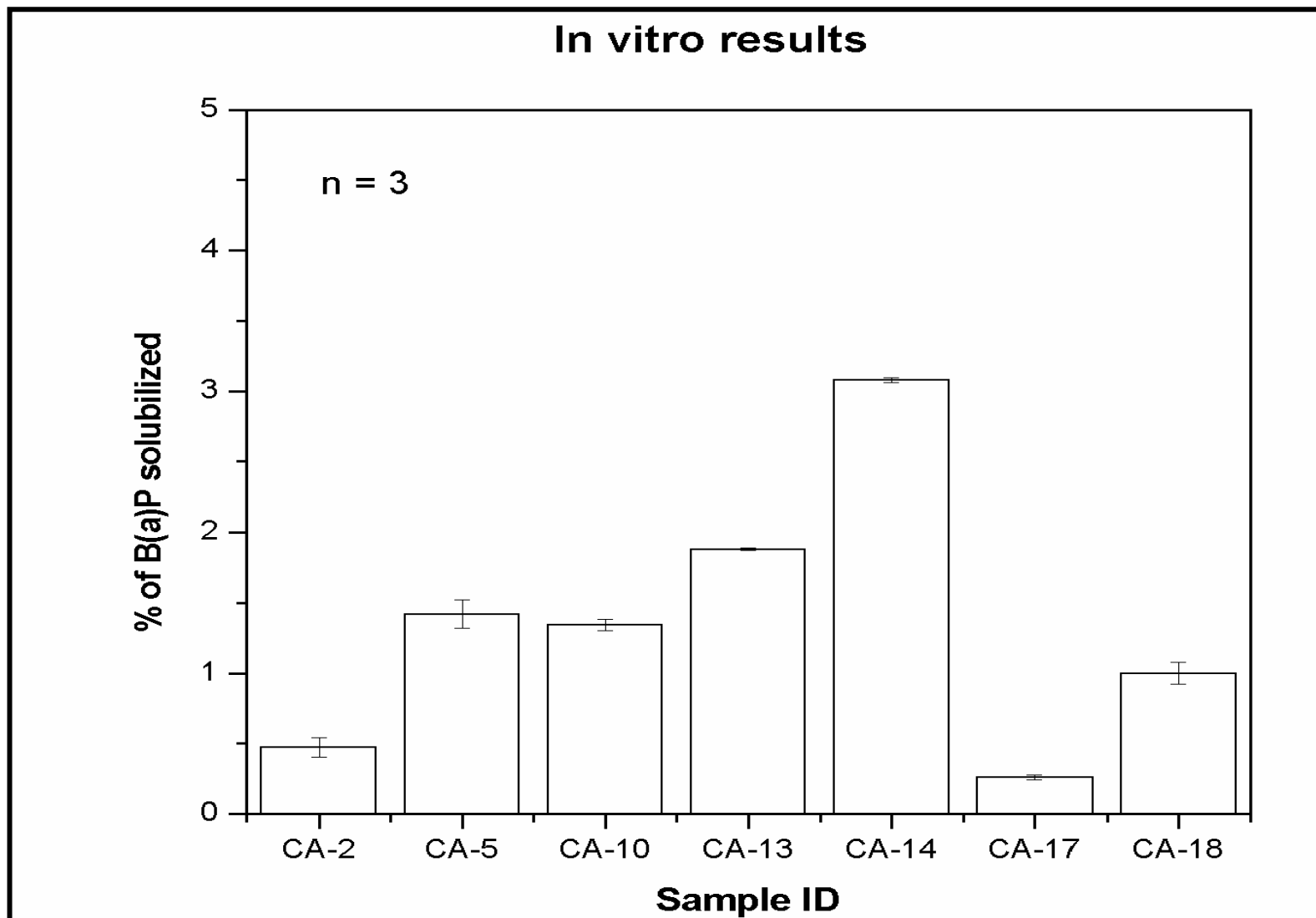
PAH	<u>% Uptake By Worms</u>		% Relative Bioavail'y
	Native	Spiked	

Naphthalene	0.01	0.04	25
Fluorene	0.02	0.08	26
Anthracene	0.01	0.23	6
Pyrene	0.06	0.98	6
Benzo[a]Anth.	0.06	1.39	5
Benzo[a]Pyrene	0.06	0.82	7

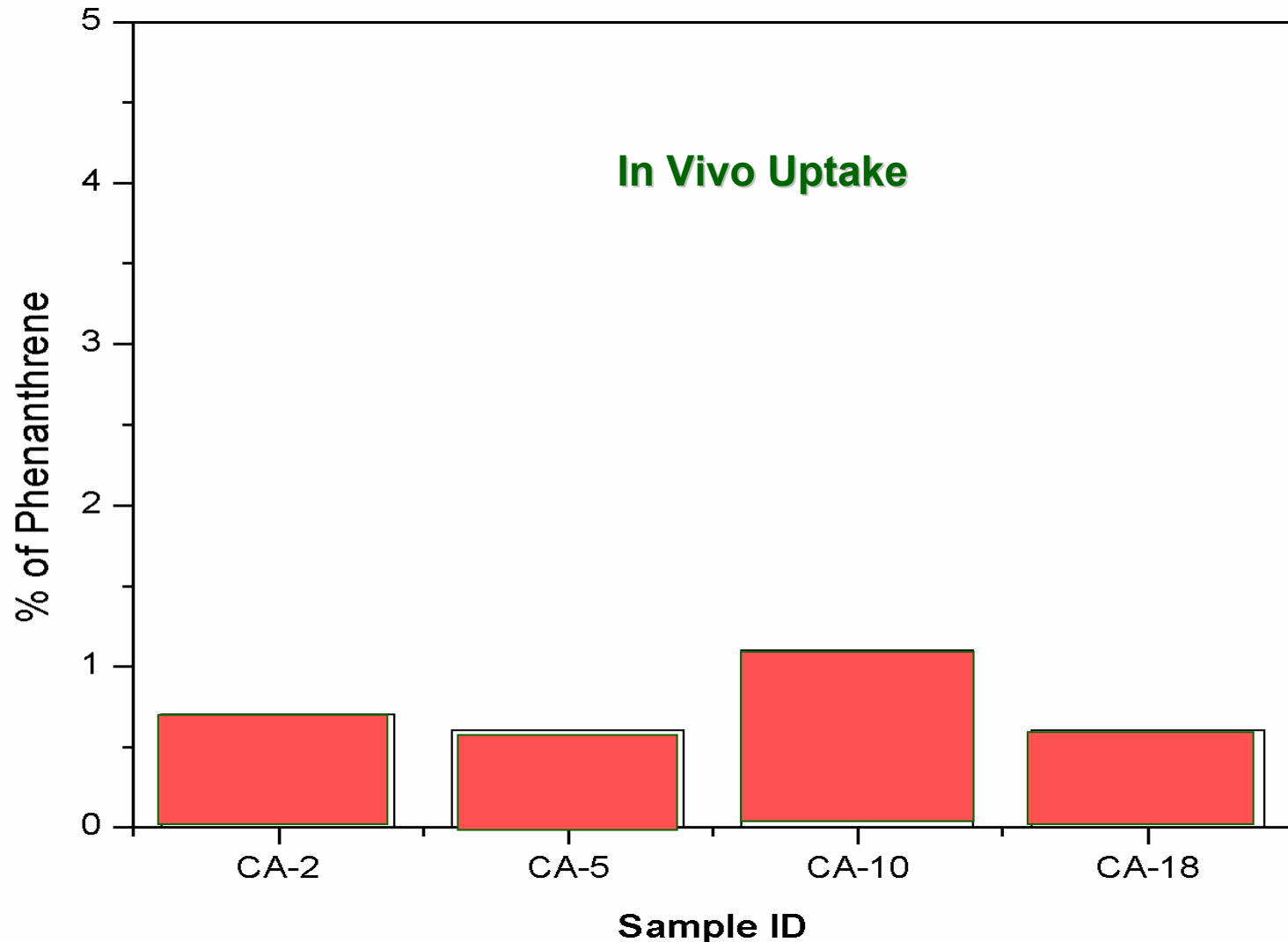
The % of B[a]P Absorbed by Skin Is 14-100x Less than CA Default



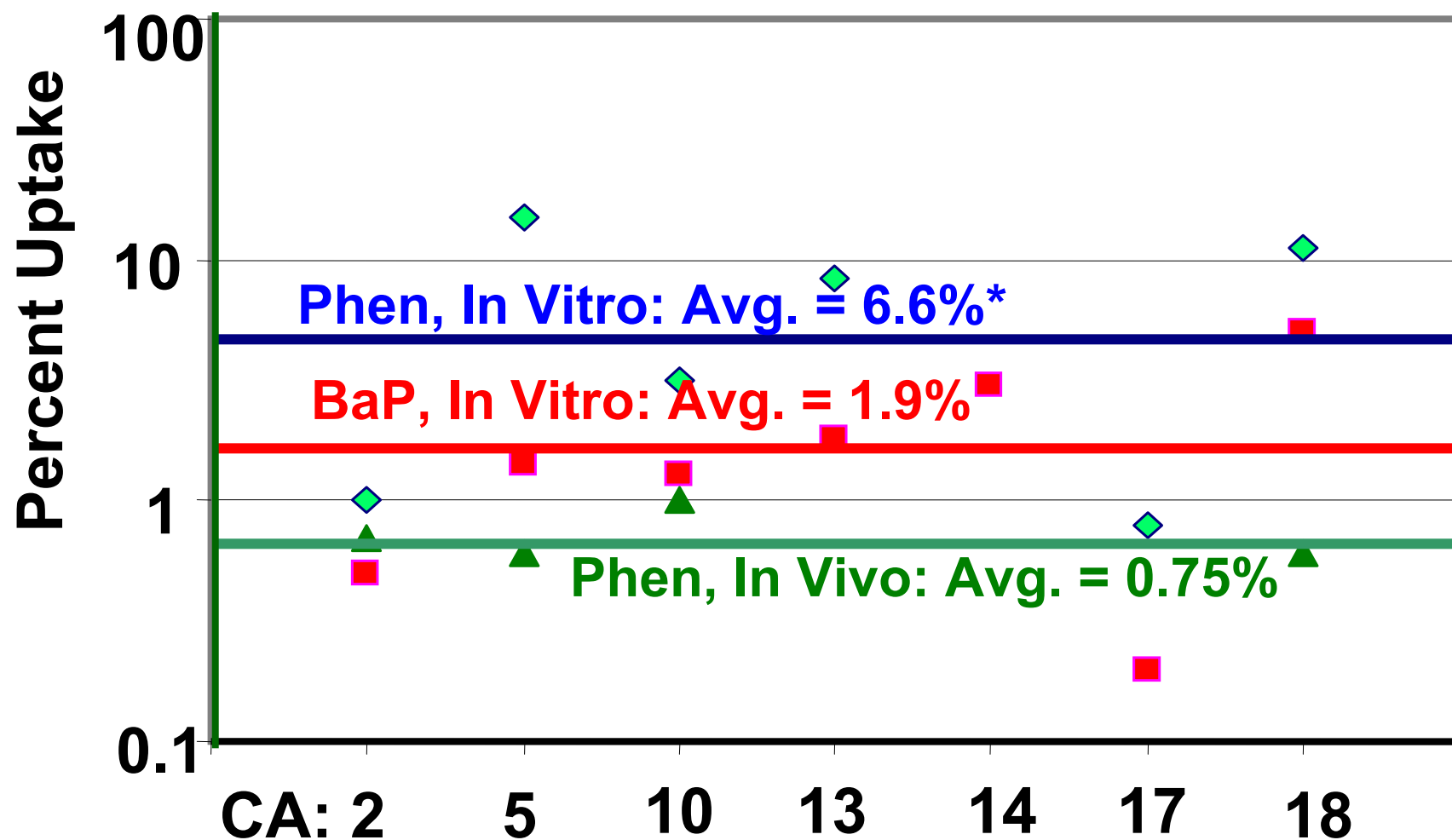
The % of B[a]P Absorbed in Simulated GI Tract Studies is Less Than 5%



The % of Phenanthrene Absorbed by Mice Is Less Than 1%



In Vivo and *In Vitro* Uptake of Phenanthrene (Phen) and Benzo(a)Pyrene (BaP)



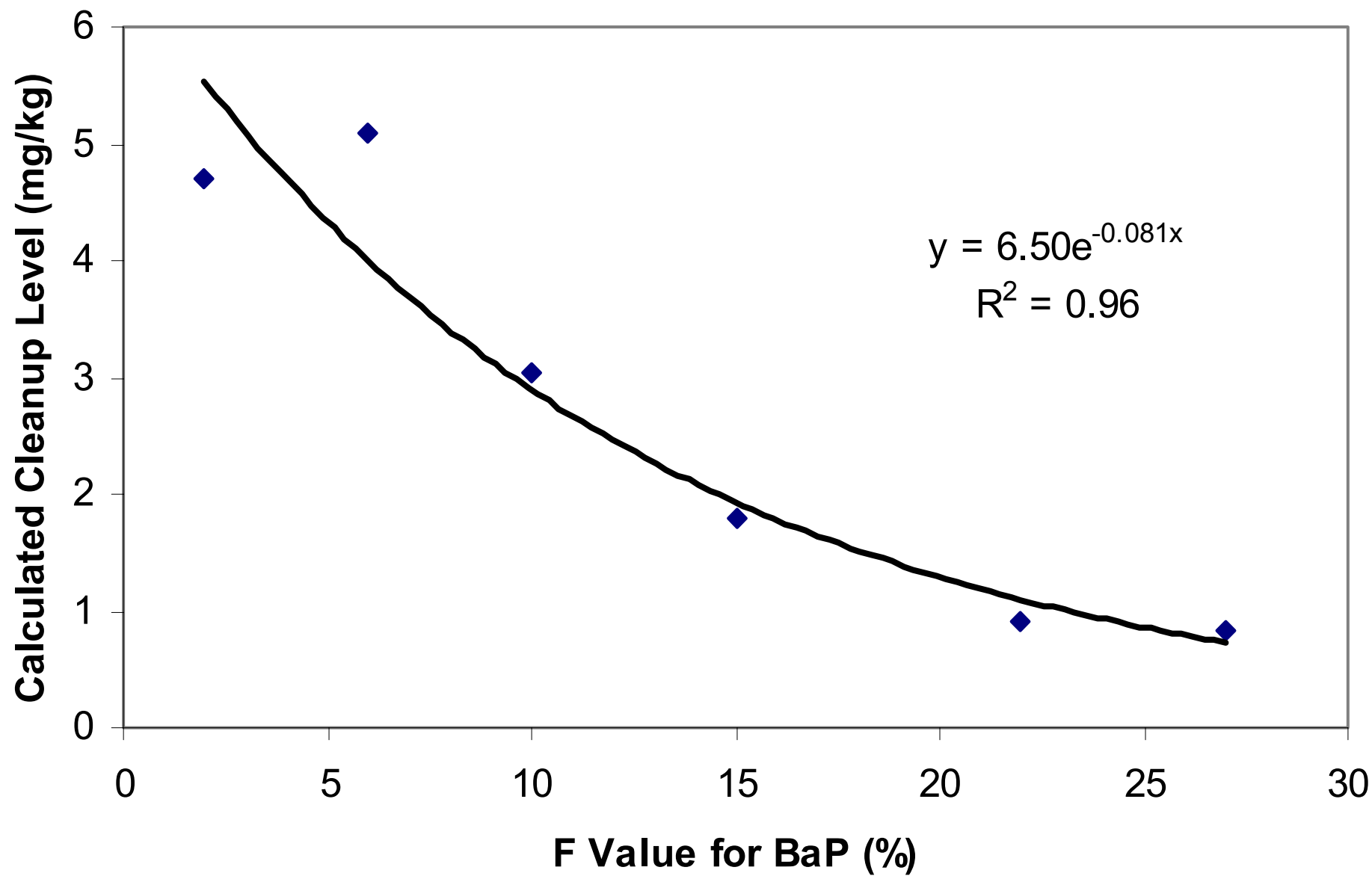
**In Vitro* Uptake of Phen in 4 *In Vivo* Samples = 7.6%

CORRELATIONS OF IN VITRO UPTAKE TO TOTAL AND SFE-DERIVED AVAILABLE CONCENTRATIONS

PAH COMPOUND	R ² VALUES	
	AVAILABLE	TOTAL
NAPHTHALENE	0 .939	0.866
ACENAPHTHENE	0 .891	0.354
FLUORENE	0 .984	0.747
PHENANTHRENE	0 .647	0.434
ANTHRACENE	0 .870	0.529
FLUORANTHENE	0 .728	0.678
PYRENE	0 .760	0.707
BENZ[A]ANTHRACENE	0 .786	0.435
CHRYSENE	0 .900	0.626
BENZO[B,K]FLUOR	0 .986	0.454
BENZO[A]PYRENE	0 .924	0.629
DIBENZ[A,H]ANTHRACENE	0 .680	0.007
BENZO[G,H,I]PERYLENE	0 .884	0.442
INDENO[1,2,3-CD]PYRENE	0 .883	0.348

Site-Specific Risk Based Criteria

Sample	Risk Based Level (mg BaP equiv./kg)	Increase
CA2	5.1	142
CA5	1.6	44
CA10	3.0	83
CA13	1.8	50
CA14	0.83	23
CA17	4.7	131
CA18	0.92	26
Mean	2.6	72
Default	0.036	-



CONCLUSIONS

Dermal uptake of B[a]P from lampblack is 1% or less, compared to the default assumption of 15%

Simulated GI tract uptake of B[a]P from lampblack is 5% or less (default assumption is 100%)

Worm uptake of PAHs from lampblack is far less than predictions based on the standard method

Proposed protocol yields risk-based cleanup levels for CPAH in lampblack of 0.8 to 5 mg/kg, 23 to 142 times higher than default criteria

SFE or ROR can be used to predict cleanup criteria based on bioassays

RECOMMENDATIONS

- **Matrix-Specific Default Criteria for Lampblack**
 - **10x Lower Availability than Assumed**
- **Protocols for Site-Specific Evaluations**
 - **Supercritical Fluid Extraction,**

And Possibly One or More Tests:

 - ***In Vitro* Simulated GI Tract Extractions**
 - ***In Vitro* Dermal Uptake Tests**
 - **Improved Leachability Assays**

Proposed Modifications to Current California (DTSC) PAH Cleanup Levels

Dermal Absorption Factor (DAF):	24-Hour Dermal Uptake Roy Protocol
Ingestion Absorption Factor (IAF):	Based on <i>In Vitro</i> Uptake Holman Protocol
Exposure / Inhalation:	No adjustment

Lessons Learned

- **Time can be reduced if phased approach is not used in the future**
- **Oral bioavailability methods require more work and validation**
- **One to two order of magnitude increases in CPAH risk-based criteria are possible**
- **Bioassays remain time-consuming, costly, and difficult to interpret**

Data Gaps

- **In Vitro / In Vivo Oral Uptake**
 - Partial metabolism caused poor mass balance
 - Baseline oral bioavailability is critical parameter
- **Measurement / Analysis**
 - Analysis of very low concentrations needed to evaluate field samples near cleanup levels
- **Applicability to Other Matrices**
 - Lampblack similar to soots
 - Binds hydrocarbons more tightly than most matrices

Acknowledgements

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In Vitro GI Tract Uptake of BaP Correlated to SFE Available Fraction.

